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7**Fluid Phase Equilibria** 356 **(2013)** 102–108 **Contents lists available at ScienceDirect Fluid Phase Equilibria journal homepage: www.elsevier.com/locate/fluid**

9**Measurement and mathematical modeling of solubility of buttery-odor substance (acetoin) in supercritical CO2 at several pressures and temperatures** **Chintya** Effendia,1, **Margareth** Shantya,1, **Yi-Hsu** Jub,∗, **Alfin** Kurniawana, **Meng-Jiy** Wangb, **Nani** Indraswatia, **Suryadi**

Ismadjia,∗∗

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article info Article history: Received 13 February 2013 Received in revised form 12 July 2013 Accepted 15 July 2013 Available online 26 July 2013 Keywords: Acetoin Solubility Density-based model Equations of state Mixing rules abstract The solubilities of acetoin (3-hydroxy-2-butanone), a frequently used buttery-odor compound in super- critical carbon dioxide (SC-CO2) at several pressures and temperatures were measured in this work. The measurements were conducted in a static-analytic mode at several pressures ranging from 8 MPa to 28 MPa and four temperatures of 313.15 K, 323.15 K, 333.15 K, and 343.15 K. The equilibrium was established for 3–4 h. The solubilities of acetoin in SC-CO2 increased with increasing both pressure and temperature beyond the crossover pressure at 8 MPa. Two

6density-based models namely Chrastil and Del Valle-Aguilera

and

1Peng–Robinson equation of state (PR-EOS) with quadratic and Stryjek–Vera mixing rules

were used to represent experimental solubilities and to describe phase behavior of the system. Both Chrastil and Del Valle-Aguilera models were able to correlate experimental solubility data satisfactorily with absolute average relative deviation (AARD) of 0.27%. Similarly, the phase equilibrium behavior of acetoin + supercritical CO2 binary system can be well interpreted by PR-EOS with quadratic (AARD of 0.11%) and Stryjek–Vera mixing rules (AARD of 0.08%). 1. Introduction Currently, food and beverage industries are growing rapidly because of the increasing demand from the market and their impor- tance for sustaining the economic growth of country. In this modern age, human needs for foods are not limited to only staple foods, but also on the processed food products. A large variety of processed food products and beverages have been well-known, such as but- ter, milk, cheese, coffee, pickles, and cookies. For attracting the consumers, most of the manufacturers use flavorings to impart a distinctive organoleptic in their food products. Acetyl methyl carbinol, commonly known as 3-hydroxy-2-butanone or acetoin, is a colorless or pale yellow liquid that is frequently used in the production of powdered flavorings for yoghurt, coffee, milk, and butter, as well as an additive in the pharmaceuticals and chem- icals manufacturing [1]. This substance has a somewhat creamy taste and a pleasant buttery-odor that can be found in several fruits ∗ Corresponding author. Tel.: +886 2 27376612; fax: +886 2 27376644. ∗∗

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035 and vegetables, such as apple, grape, broccoli, blackcurrant, and strawberry. Acetoin is also produced from the metabolic activity of glucose by a number of fermentative bacteria such as Enterobacte- riaceae, Bacillus, and Leuconostoc sp. [2–4]. In recent years, research devoted to the applications of super- critical fluids (i.e., the fluids that exhibit a gas-like mass transfer rate and a liquid-like solvent power) for diverse applications, such as fractionation [5], extraction [6], reactions [7], biotechnology advances [8], production of fine chemicals [9], and nanomaterials processing [10] becomes increasingly popular. The main advan- tages of using supercritical fluids (SCFs) are the tunable solvation power by manipulating pressure and temperature and highly selec- tive dissolution ability without damaging or contaminating the target compound. Carbon dioxide (CO_2) is by far the most exten- sively used supercritical solvent, owing to its practical advantages, such as cheap, readily available in high purity, safe handling and storage (non-flammable and non-explosive), environmentally friendly, has relatively low critical pressure (7.38 MPa) and criti- cal temperature (304.25 K), and ease separation from the product. Furthermore, carbon dioxide is regarded as a non-toxic substance based on The U.S. Food and Drug Administration (FDA) approval [11]. When dealing with the effective design and optimization of supercritical-based processes of flavorings for scale-up operation, the knowledge about equilibrium solubility data of solute in super- critical solvent over a wide range of pressures and temperatures are of crucial importance. In the present work, the solubilities of acetoin in co-solvent free supercritical CO_2 (SC-CO_2) were experimentally measured using a static-analytic method at elevated

17**temperatures from** 313 **.15 K to** 343 **.15 K** and several **pressures** ranging **from** 8 **MPa to** 28 **MPa.**

Previous research dealing with acetoin only attempted to isolate and identify this volatile compound from various food- stuffs and beverages, such as rice cakes [12], raw and cooked pine-mushrooms [13], kefir [14], beer [15], wine [16], and marine animals [17–19], using the combination of headspace solid-phase microextraction (SPME) and gas chromatography–mass spectrom- etry (GC–MS) techniques. The supercritical CO_2 extraction and process optimization for the recovery of various aroma-active com- pounds in Zhenjiang aromatic vinegar has been carried out by Lu and colleagues [20]. To the best of our knowledge, the sol- ubility measurement and the evaluation of phase behavior of acetoin + supercritical CO_2 system is not available in the literature. Because acetoin has a fairly low dipole moment (i.e., 2.35) and CO_2 behaves as a lipophilic solvent in supercritical state, there- fore acetoin is readily soluble in supercritical CO_2 and the addition of modifiers (co-solvent) is not required.

21**The solubility data** are **correlated by** two **density-based** models (i.e., **Chrastil and Del Valle−Aguilera)**

and phase equilibrium behavior of the system were investigated by

1**Peng–Robinson equation of state with quadratic** and Stryjek–Vera **mixing rules.**

2. Materials and methods 2.1. Chemicals Acetoin (purity 98%, Tm = 15 ◦C, CAS Number: 513-86-0) was purchased from Sigma–Aldrich, Singapore as crystalline dimer form with molecular weight of 88.11 g/mol and used without fur- ther purification. Liquid carbon dioxide (99.98% pure) was supplied by Aneka Gas Pty Ltd. as food grade in a dip-tube supply cylin- der. Ethanol (96%, Sigma–Aldrich) was used as a liquid medium for trapping acetoin. 2.2. Solubility measurements The solubilities of acetoin in supercritical CO2 at various pressures and temperatures were experimentally measured in a bench-scale supercritical apparatus using static-analytic method [21,22].

26**The schematic diagram of** equipment set-up **is shown in Fig. 1.**

5**The maximum working pressure and** working temper- ature **of the system are** 40 MPa **and** 423 **.15 K, respectively.**

All tubings and fittings are made

2**from 316SS-grade stainless steel** (Swagelok). Briefly, **a**

piece of cotton (±1 g) was wetted with liquid acetoin (1 ml) and packed in a 150 cm3 high-pressure double-ended equilibration cylinder. The system was evacuated thereafter by a vacuum pump (GAST DOA-P504-BN). The system was heated from room temperature to desired temperatures (313.15 K, 323.15 K, 333.15 K, and 343.15 K) using a thermostated oven. Then, liquid CO2 was compressed and delivered to the equilibration cylinder using an Eldex AA-100-S-2 horizontal reciprocating pump with dual inlet ports by opening valve V-1. The flow rate of liquid CO2 was held constant at 10 ml/min until the preset pressure was reached. To maintain isothermal and isobar conditions, the system

10**pressure was monitored real-time by a** digital **pressure**

indicator connected to pressure transducer (Druck PTX 611) and the system temperature was controlled with uncertainties of ±1 K. Prelimi- nary experiments showed that equilibrium was established within 3–4 h. The equilibrated supercritical phase was swept out from the sample cylinder at the same condition by fresh

CO_2 into a receiving vial filled with 100 ml 96% ethanol. Ethanol was used as a trapping solvent because it can readily dissolve acetoin, cheap, and safer than methanol. Care was taken to prevent sample precipitation during depressurizing high-pressure stream by gently heating the discharge line. The receiving vial was equipped with a vent needle

11**to allow the expanded gas to exit and**

11**total volume of solute-free ambient gas was** recorded using **a calibrated wet gas flow meter** (ZEAL DM3B) **at a known** pressure **and**

temperature (±0.05 L). The ethanol containing acetoin was subjected to gas chromatography for analysis. The mass of cotton was weighed before and after each experimental run. All experimental data were reproduced by three replicate experiments at the identical conditions and presented as mean ± SD (n = 3). 2.3. Analysis of acetoin content The concentration of acetoin in the trapping solvent (wt%) was quantified by gas chromatography technique on a Shimadzu GC- 2014 equipped with a split/splitless injection port and a flame ionization detector (FID). The stationary phase was

10**an Agilent DB-** 1 dimethylpolysiloxane **capillary column (30 m**

× 0.53 mm × 3 ?m). Fig. 1. Experimental set-up for solubility measurement (Dip-tube liquid CO_2 cylinder (1); Reciprocating pump (2); Pressure transducer (3); Thermostated oven (4); High- pressure equilibration column (5); Receiving vial (6)). = 0.3789 + 1.4897ω − 0.1√713ω2 + 0.0196ω3 √ ˛(Tr, ω) = ((1 + (+ 1(1 + Tr) (0.7 − Tr))(1 − Tr))) [23]: was calculated by the following equation: 2 (9) (8) parameters and changing the polynomial fit of the acentric factor data by introducing two additional adjustable pure compound model's accuracy for predicting the vapor-liquid equilibria (VLE) and Vera (1986) on Peng–Robinson equation of state improved the respectively. The mathematics modification proposed by Stryjek tric factor for pure carbon dioxide is 7.39 MPa, 304.25 K, and 0.225, compound. The critical pressure, critical temperature, and acen- tric factor and is an adjustable parameter characteristic of each of operating temperature to critical temperature, ω is the acen- compound at critical point, Tr is reduced temperature or the ratio where Pc and Tc are pressure (MPa) and temperature (K) of the pure b = 0.0778 RPTcc = 0.3746 + 1.5423ω√− 0.2669ω2 ˛(Tr, ω) = (1 + (1 − Tr)) ˛ = 0.4572R2PTcc2 a(T) = ˛.˛(Tr, ω) 2 For pure component system, a and b values are given as follows: constant (8.314 J/mol K), a(T) and b are Peng–Robinson constants. (dm3/mol), T is the absolute temperature (K), R is the universal gas where P is the absolute pressure (atm), V is the molar volume P y = V − RT b − V 2 + 2bV − b2 a(T) ematical form [24]: (7) (6) (5) (4) (3) (2) original

20**Peng–Robinson equation of state** has **the** following math- **equation of state**

[23] and the results are tabulated in Table 1. The culated by Peng–Robinson with Stryjek–Vera modification (PRSV) supercritical CO_2 at various pressures and temperatures were cal- depend on the applied pressure and temperature. The densities of ability to be a gas-like and solvent power to be a liquid-like strongly properties of supercritical fluids associated to their penetration Generally speaking about supercritical fluids

(SCFs), the tunable 3.1. Solubilities of acetoin in supercritical CO2 3. Results and discussion of CO2 (44.01 g/mol) and acetoin (88.11 g/mol), respectively. to the equilibration cylinder (L), M1 and M2 are the molecular mass liquid CO2 at 303.15 K (g/L), V1 is the volume of liquid CO2 supplied is the mass of acetoin in trapping solvent (g), 1 is the density of where y2 is the mole fraction of acetoin in supercritical CO2, m2 2 (1V1/M1) (m2/M2) (1) to 20 mg/l. The solubility of acetoin, in the unit of mole fraction, tions of acetoin with different concentrations ranging from 1 mg/l calibration curve was prepared by measuring five standard solu- 28

2**min. The injection volume was 1** ?l **with a split ratio of** 10:1. **The**

and a final isotherm at 260 ◦C for 1 min. Total program time was 40 ◦C for 5 min, followed by a first ramp to 260 ◦C at 10 ◦C/min, temperature of 250 ◦C; (4) temperature profile of the column oven: ity of 30 cm/s; (2) detector temperature of 300 ◦C; (3) injection port phase (carrier gas): Helium at 29.4 kPa and a constant linear veloc- The analysis conditions were given in detail as follows: (1) mobile 104 Table 1 Experimental solubilities of

22**acetoin in supercritical CO2 at several pressures and temperatures.** C. **Effendi**

et al. / Fluid Phase Equilibria 356 (2013) 102–108 P (MPa) 313.15 K 323.15 K 333.15 K 343.15 K CO2a (g/L) y2b (×10−5) Sc (×10

25**−2 g/L) CO2 (g/L)**

y2 (×10−5) S (×10

25**−2 g/L) CO2 (g/L)**

y2 (×10−5) S (×10

25**−2 g/L) CO2 (g/L)**

y2 (×10−5) S (×10−2 g/L) 8 284 10 565 12 667 14 726 16 768 18 802 20 830 22 855 24 876 26 895 28 913 0.68 ± 0.03 1.74 ± 0.09 2.20 ± 0.14 2.38 ± 0.07 2.69 ± 0.15 2.82 ± 0.08 2.91 ± 0.15 3.02 ± 0.11 3.17 ± 0.12 3.30 ± 0.05 3.33 ± 0.21 0.39 ± 0.02 1.96 ± 0.08 2.93 ± 0.18 3.46 ± 0.09 4.13 ± 0.14 4.53 ± 0.22 4.84 ± 0.16 5.16 ± 0.19 5.55 ± 0.24 5.90 ± 0.15 6.08 ± 0.07 225 0.98 ± 0.05 376 1.99 ± 0.08 535 3.12 ± 0.15 625 3.94 ± 0.23 684 4.62 ± 0.19 728 4.70 ± 0.14 764 5.23 ± 0.27 794 5.31 ± 0.21 819 5.62 ± 0.16 842 5.99 ± 0.26 862 6.43 ± 0.32 0.44 ± 0.04 1.50 ± 0.03 3.33 ± 0.11 4.93 ± 0.18 6.32 ± 0.15 6.84 ± 0.23 7.99 ± 0.15 8.44 ± 0.26 9.20 ± 0.17 10.10 ± 0.14 11.09 ± 0.08 196 1.51 ± 0.12 293 2.58 ± 0.06 415 4.36 ± 0.09 521 6.07 ± 0.18 596 7.05 ± 0.08 652 7.81 ± 0.25 695 8.47 ± 0.22 731 9.56 ± 0.36 761 9.60 ± 0.04 787 9.87 ± 0.17 811 10.84 ± 0.41 0.60 ± 0.02 1.51 ± 0.09 3.62 ± 0.18 6.33 ± 0.12 8.40 ± 0.15 10.20 ± 0.28 11.78 ± 0.24 13.98 ± 0.19

14.61 ± 0.36 15.53 ± 0.21 17.58 ± 0.32 178 251 342 435 514 577 627 668 703 733 759 2.36 ± 0.14 3.87 ± 0.07 5.91 ± 0.05 7.97 ± 0.03 10.53 ± 0.34 12.58 ± 0.27 13.36 ± 0.16 15.22 ± 0.44 15.83 ± 0.39 17.71 ± 0.28 18.30 ± 0.17 0.84 ± 0.04 1.94 ± 0.11 4.04 ± 0.26 6.93 ± 0.19 10.83 ± 0.31 14.52 ± 0.28 16.76 ± 0.14 20.34 ± 0.07 22.26 ± 0.34 25.97 ± 0.21 27.80 ± 0.27 a Predicted by PRSV equation of state [23]. b Mole fraction of acetoin in supercritical CO2. c Solubility of acetoin in supercritical CO2. The value of 1 can be conveniently assumed to be zero for most compounds [23]. The application of PRSV equation of state is gener- ally superior to other equations of state in predicting the densities of various compounds, particularly the nonpolar ones and only requires little computer resources to solve the equation. As shown in Table 1, the densities of supercritical CO2 increased at higher pressures for constant temperature, which also means greater sol- vent power of the fluid.

4**A plausible explanation to this point is that**

increasing pressure would reduce the available volume occu- pied by the molecules so the molecules become closer each other. Accordingly, the ratio of mass to volume becomes higher at higher pressures and therefore the density of CO2 rose. Meanwhile, the densities of supercritical CO2 decreased with increasing temper- ature at constant pressure. This might be attributed to greater molar volume (Vm) at elevated temperatures. Since the density and molar volume is inversely proportional hence the increasing value of molar volume leads to lower value of density and vice versa. The solubilities of acetoin in SC-CO2 increased with increas- ing both pressure and temperature (Table 1). At temperature of 313.15 K, the increase of pressures from 8 MPa to 16 MPa enhanced the mole fraction of acetoin in SC-CO2 from (0.68 ± 0.03) × 10−5 to (2.69 ± 0.15) × 10−5. Similar trends were observed in three other temperatures studied. This might be attributed to enhanced solvent power of the fluid toward solute at elevated pressures and tempera- tures. Moreover, an isobaric increase in temperature gave a positive effect on the solubilities of acetoin in supercritical CO2. As can be seen, the mole fraction of acetoin in SC-CO2 at 20 MPa increased progressively from 2.91 × 10−5 to 13.36 × 10−5 with temperature rise from

14**313.15 K to 343.15 K.** These **results**

confirm the signifi- cance of vapor pressure of solute toward solubilities at pressures beyond the crossover point (8 MPa) in which the solute tends to become more volatile at higher temperatures, allowing more acetoin to dissolve in supercritical CO2. Furthermore, increasing temperature may also improve diffusivity (or mass transfer rate) of solute to the solvent phase thus higher solvated amounts of acetoin in supercritical CO2. 3.2. Correlations of experimental solubility data and phase equilibria

2**With regards to** process **design and optimization of supercritical-**

based technologies for industrial applications, particularly in food and flavorings industries, the knowledge about equilibrium concentration of acetoin in the solvent phase

4**over wide range of pressures and temperatures** are essentially needed. **For** this purpose, the phase equilibria of acetoin in supercritical carbon dioxide were evaluated using two sorts of approaches: (1) density-based correlations and (2) theoretical cubic equations of state. The density-based correlations were commonly developed semi-empirically based on simple error minimization between actual and predicted values either using least-square or nonlinear regression techniques. The correlation of actual solubility data by density-based models offers an advantage because it does not require thermophysical properties of the compounds of interest such as molar volume, acentric factor, and critical point that normally cannot be measured from experiment. 3.3. Density-based correlations In the present work, two popular semi-empirical

6**density-based models** namely **Chrastil and Del Valle-Aguilera**

equations were applied to correlate experimental solubilities of

22**acetoin in** SC **-CO2 at several pressures and temperatures.**

Chrastil (1982) was the first who proposed density-based model by assuming that a solvato complex was formed between solute and supercritical solvent at equilibrium state, as described below [25]: X + kY ↔ (XYk) (10) From Eq. (10), it can be seen that one molecule of solute X asso- ciates

24**with k molecules of supercritical solvent** Y **to form solvato**

complexes (XYk) at equilibrium. The value of parameter k is not an integer in most cases based on the fact that the formation of solvato complex is not occurred stoichiometrically in which some of them become less or more stable [25]. Therefore, parameter k is often designated as an average association number for a given solute-supercritical solvent system. Chrastil model relates the solu- bilities of solute in supercritical solvent to that of solvent density and operating temperature in the following expression: c = k exp a

19**T + b** (11) **where** c **is the solubility of solute (kg/** m3), **is the** solvent **density**

( ) (kg/m3),

21**T is** the **absolute temperature (K),** a **is a**

function of enthalpy of solvation (?Hsolv) and enthalpy of vaporization (?Hvap), and b is a function of average association number that depends on the molecular mass of solute and supercritical solvent. The values of adjustable parameters k, a, and b are specific for each solute- supercritical solvent pair and not dependent on temperature and pressure. These parameters were simultaneously

4**determined by** performing **nonlinear regression fitting of the** model toward actual solubility data

4**using SigmaPlot software (Version 12.3, Systat** Soft- ware **Inc.).**

In order to minimize the error between actual and predicted solubilities, the following objection function (OF) was applied: N OF = yicalc − yiexp (12) ∑i yiexp

18**where N is| the number |of experimental data,** yicalc **and** yiexp **are** the calculated **and** experimental **solubility values, respectively.**

The second semi-empirical density-based correlation used was

15**Del Valle and Aguilera equation.** They studied **the**

solubilities of

15**vegetable oils in** dense **CO2** and **took into account the change** in enthalpy **of vaporization with temperature** by assuming **the** independency of average **association**

number toward density and temperature [26]. Del Valle and Aguilera model, which is analog to Chrastil model, has a mathematical form as follows [26]: c = k exp b + a + d T T 2 (13) The agreement of both models in correlating experimental sol- ( ) ubility data was assessed from the corresponding absolute average relative deviation (AARD), defined as follows: AARD (%) = 100 N yiexp (14) N yicalc − yiexp ∑i=1 | The three-dimens|ional fittings| of

6**Chrastil and Del Valle** and **Aguilera models** against experimental **solubility**

data of acetoin in SC-CO2 as a function of temperature and solvent density are shown in Fig. 2. The dot symbol and wire-mesh line represent experimental data and the model fit, respectively. The fitted param- eter values of Chrastil and Del Valle and Aguilera models are listed in Table 2. From Fig. 2, it can be seen that both models satisfactorily representing experimental solubilities with the abso- lute average relative deviation of 0.27% for both Chrastil and Del Valle and Aguilera models. The average association number (k) regarding the formation of solvato complex between acetoin and supercritical CO2 was 2.42 for both models. This means that one 106 C. Effendi et al. / Fluid Phase Equilibria 356 (2013) 102–108 Fig. 2. Three-dimensional fittings of Chrastil (a) and Del Valle and Aguilera (b) correlation models toward experimental solubilities of acetoin in supercritical CO2. Table 2 The adjusted constant

6**parameters of Chrastil and Del Valle** and **Aguilera** models **for** acetoin (1) + supercritical CO2 (2) system. T (K) Chrastil a b k AARD (%) Del Valle and Aguilera a b d k AARD (%) 313.15 323.15 333.15 −7,005.70 3.08 2.42 0.27 −11,237.87 9.46 7.01 × 105 2.42 0.27 343.15 molecule of acetoin associates with 2.42 molecules of supercrit- ical CO2 to form a solvato complex at equilibrium. As aforesaid, the adjustable parameter a is a function of enthalpy of solva- tion (?Hsolv) and enthalpy of vaporization (?Hvap), expressed as a = ?Hsoln/R for Chrastil model and a = (Hsolv/R) − (2d/T) for Del Valle and Aguilera model where ?Hsoln is total heat of reac- tion or enthalpy of solution (i.e., ? Hsoln(= ?Hsolv + ?Hvap). It)was found that total reaction heat to form acetoin-supercritical CO2 sol- vato complexes was negative, indicating the feature of a non-ideal solution system and an exothermic dissolving process of solute in supercritical solvent. The negative value of total reaction heat may also be implicit information about greater magnitude of heat released from the associating process between acetoin and SC-CO2 molecules to form solvato complexes than that required for the break down of intermolecular forces of solute and supercritical sol- vent molecules. The total heat of reaction for Chrastil model was −58.25 kJ/mol, which is comparable to that of Del Valle and Aguilera model (?Hsoln = −57.87 kJ/mol). The values of adjustable parame- ter b, defined as b = ln (M1 + kM2) + q − k ln M2 should be similar for two models because this parameter is a function of average associ- ation number (k) and molecular weight of solute (M1, 88.11 g/mol) and supercritical solvent (M2, 44.01 g/mol). However, the fitted val- ues of parameter b for Chrastil and Del Valle and Aguilera models are significantly different (i.e., 3.08 for Chrastil and 9.46 for Del Valle and Aguilera). This may be attributed to the inclusion of new adjustable parameter (d/T2) in Del Valle and Aguilera correlation model to compensate for the variation of the solute’s vaporizing heat with temperature that leads to higher magnitude of constant q (i.e., 6.97 for Chrastil model vs. 13.35 for Del Valle and Aguilera model). 3.4.

12**Cubic equations of state The** phase equilibria **of**

acetoin-supercritical CO2 system at various pressures and temperatures were studied based on the theoretical approach of cubic equations of state. The critical properties (Pc and Tc) and acentric factor (ω) of pure acetoin were predicted by Joback and Lee-Kesler group contribution method [27], respectively and the results are given as follows: Tc of 629.92 K, Pc of 6.27 MPa and ω of 0.53. In this regard,

1**Peng–Robinson equation of state with quadratic** and Stryjek–Vera **mixing rules**

was applied for evaluating phase behavior of acetoin + supercritical CO2 mix- ture at equilibrium. The cross coefficients

20**a and b of Peng–Robinson equation of state for**

binary component systems can be expressed in the form of one-fluid mixing rule as follows: a =

12**N N xi xj aij ∑i=1∑j=1** (15) b = **N N xi xj bij ∑i=1∑j=1**

(16) The values of adjusted

8**binary interaction parameters** aij **and** bij **were determined**

by applying appropriate mixing rules. For this purpose, the classical quadratic mixing rule was selected to deter- mine the adjusted mixing parameters aij and bij [28]: aij = aiaj × (1 − kij) with kij = kij (17)

23**bij = √bi+ bj 2 × (1 lij) with lij lji**

− = (18) where ai, aj,

5**bi, and bj are the Peng–Robinson parameters for pure**

component that can be determined from Eqs. (3) and (5), respec- tively by introducing parameters ˛(Tr,ω) and for

26**PRSV equation of state. The** following Stryjek–Vera **mixing rule was**

also employed Input data of component properties (Tc, Pc, Tb) and solubility of acetoin Choose Peng-Robinson EOS Trial kij and lij Quadratic Mixing rule Stryjek-Vera Trial kij, kji and lij No OF = minimized OF = minimized No Yes Yes Obtain value of kij and lij Obtain value of kij, kji and lij Fig. 3. The computational algorithm for determining binary interaction parameters (kij, kji, and lij) of Peng–Robinson equations of state with quadratic and Stryjek–Vera mixing rules. for the prediction of adjusted binary interaction parameters aij and bij [29]: kij kji aij = aiaj × 1 − xikij xjkji with kij =/ kij (+)

23**bij = √bi+ bj 2 × (1 lij) with lij lji**

− = (19) (20) Here,

8**xi and** xj **represent the** mole **fraction of**

solute and supercritical solvent in the binary mixture, respectively. The values of adjusted

8**binary interaction parameters (kij,** kji, **and lij) were determined**

following algorithm described in Fig. 3 using PE2000 computational software (Version 2.9.9a). The computation was started by inputting the critical properties of pure compo- nent and adjusting the values of mixing parameters kij, kji, and lij until convergence and minimized objective function satisfied. The predicted compositions of acetoin in supercritical CO_2 with optimized binary interaction parameters are plotted against actual data in Fig. 4. The change of temperatures slightly increases the values of binary interaction parameters kij and lij (Table 3) for both quadratic and Stryjek–Vera mixing rules, indicating a weak positive dependence of these parameters toward temperature. However, the increasing values of parameters kij and lij denote that higher temperature facilitates the interaction between “like” molecules (i.e., solute

24**-solvent) to form a solvato complex.** This behavior **is** con- sistent **with the**

physical meaning of negative sign of total reaction heat obtained from density-based correlations that reflect stronger attraction forces between solute and solvent than those of solvent- solvent or solute-solute molecular interactions. The magnitude of

8**binary interaction parameters kij and lij in** this **work**

is much lower Fig. 4. Correlations between measured (dot symbols) and predicted (dashed lines) mole fraction of acetoin in supercritical CO_2 using PR-EOS with quadratic (A) and Stryjek–Vera (B) mixing rules. 108 C. Effendi

7**et al. / Fluid Phase Equilibria** 356 **(2013)** 102–108 **Table 3 The**

optimized binary interaction parameters of PR-EoS with quadratic and Stryjek–Vera mixing rules for acetoin (1) + supercritical CO_2 (2) system. T (K) Quadratic mixing rule kij lij AARD (%) kij Stryjek–Vera mixing rule kji lij ij a AARD (%) 313.15 0.115 323.15 0.116 333.15 0.118 343.15 0.119 0.066 0.133 0.067 0.135 0.069 0.11 0.137 0.070 0.138 0.420 0.042 0.412 0.043 0.394 0.044 0.356 0.044 −0.287 −0.277 −0.257 0.08 −0.218 a ?ij is calculated by subtracting kij and kji, which also equals to -?ji [29] than that obtained by Ismadji and Bhatia [30] for the solubilities of three flavor esters namely ethyl propionate (MW of 102.13 g/mol), ethyl butyrate (MW of 116.16 g/mol), and ethyl isovalerate (MW of 130.18 g/mol) in dense CO_2. This difference is possibly due to lesser asymmetry degree of acetoin + supercritical CO_2 system because solute and supercritical solvent have similarity in terms of polarity and molecular size compared to those systems in Ismadji and Bha- tia study. Additionally, the dissimilarity in molecular size between solute and solvent resulted in the negative values of mixing param- eters kij and lij, as observed in Skerget et al. [31] and de la Fuente et al. [32] study for vanillin + carbon dioxide and capsaicin + carbon dioxide system, respectively. By judging the AARD values, PR-EOS with quadratic and Stryjek–Vera mixing rules both can describe the phase behavior of acetoin + supercritical CO_2 system at studied pressures and temperatures satisfactorily and shows consistency with density-based correlation. 4. Conclusions The solubilities and phase equilibrium behavior of acetoin in supercritical CO_2 at

14**temperatures ranging from 313.15 K** to **343.15 K and** several **pressures up to** 28 **MPa** have been inves- tigated in this work. The equilibrium concentration of acetoin in supercritical CO2 ranged between (0.39 ± 0.02) × 10−2 g/L and (27.80 ± 0.27) × 10−2 g/L. Beyond the crossover pressure (8 MPa), the solubilities increased with increasing both pressure and tem- perature due to synergistic effects between solvent power and vapor pressure of solute. The endothermicity of associating process between acetoin (X) and SC-CO2 (Y) to form a solvato complex can be well interpreted by Chrastil and Del Valle and Aguilera mod- els

19**with an** absolute **average relative deviation (AARD) of 0.**

27%.

18**Total reaction heat** for the **vaporization and solvation**

of acetoin in supercritical CO2 was about −58 kJ/mol. The evaluation of phase behavior by

1**Peng–Robinson equation of state with quadratic** and Stryjek–Vera **mixing rules**

reveals a weak positive dependence of adjusted

1**binary interaction parameters kij and lij**

with tem- perature rise.

2**To this end, the present work provides** adequate information for **the**

readership regarding solubility data of acetoin

5**in supercritical** CO2 **over a wide range of** pressures **and**

temper- atures for scale-up production of this flavoring compound in the supercritical-based food, beverage, or pharmaceutical industries. Acknowledgements The first two authors (Chintya Effendi and Margareth Shanty) would like to thank

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